High Energy Rechargeable Lithium-Metal Cells: Fabrication and Integration

JIE XIAO (PI) AND JUN LIU
PACIFIC NORTHWEST NATIONAL LABORATORY

JUNE 20TH, 2018

2018 DOE VEHICLE TECHNOLOGIES PROGRAM ANNUAL MERIT REVIEW

Project ID #: Bat369

Overview

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Timeline

- Project start date: December 2016
- Project end date: October 2021
- Percent complete: 30%

Barriers

- Low energy: Li metal anode will boost cell energy
- Short battery Life: mitigating side reactions will extend the cycling stability

Budget

- Total project funding: $50M
  - DOE share: 100%
- Funding for FY 2017: $10M
- Funding for FY 2018: $10M

Partners

- Battery 500 PIs
- BNL,ARL,INL,SLAC
- 10 universities
- GM, Navitas Systems

BATTERY 500 CONSORTIUM

Relevance/Objectives

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- **Overall Objectives**
  - Overcome the fundamental issues in building high-energy rechargeable Li metal batteries
  - Demonstration of long-term cycling of 500 Wh/kg Li metal cells
- **Objectives of this period**
  - Identify the cell-level scientific challenges in high-energy rechargeable Li metal batteries: Li/NMC and Li-S
  - Demonstrate 300 Wh/kg Li metal pouch cells for at least 50 stable cycling
- **Impacts**
  - Accelerate the development of high-energy rechargeable Li metal batteries for future vehicle electrification

BATTERY 500 CONSORTIUM

Milestones: Keystone Project 3 for Cell Fabrication, Testing and Diagnosis

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Milestones and Go/No-Go Decisions	Date	Status
Investigate methods to extend the cycling and stability of Li metal pouch cells.	12/31/2017	Completed (Jason Zhang)
Develop stage 2 coin cell and stage 1 pouch cell testing protocols	3/31/2018	Completed (Jie Xiao/Eric Dufek)
Develop procedures to identify the failure of Li-metal anode in coin cells and pouch cells	6/30/2018	On track
Deliver 350 Wh/kg Li metal pouch cell (> 50 cycles and < 20% capacity fading)	9/30/2018	On track

BATTERY 500 CONSORTIUM

Approach

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

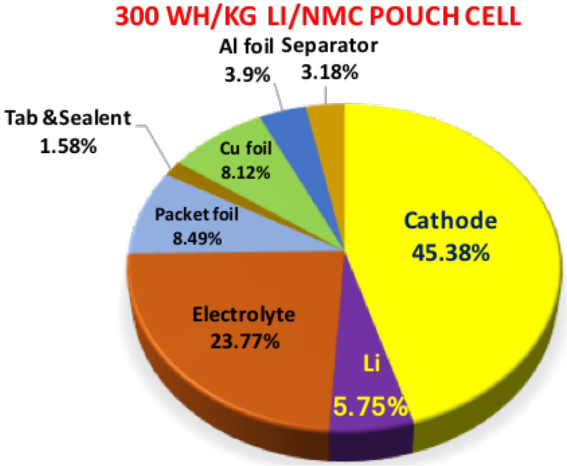
- Pouch cell design and analysis to provide a clear roadmap to build high-energy Li metal cells.
- Identify the key factors that limit the cycling of rechargeable Li metal cells
- New electrolytes and cell optimization to extend reversible cycling of lithium metal anode
- Close the gap between coin cell evaluation and pouch cell testing for fast screening of innovative and effective approaches

Technical Accomplishments

Design and Fabrication of 300 Wh/kg Li/ $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) Pouch Cell

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

	Parameters	Real Value
Cathode	Material	$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$
	1st dicharge capacity (mAh/g)	180
	Active material Loading	96%
	Coating weight (mg/cm^2 each side of Al)	21.8
	Areal Capacity (mAh/cm^2 each side of Al)	3.8
	Electrode press density (g/cm^3)	3.0
	Electrode thickness(each side of Al foil) (µm)	72
	Al foil thickness (µm)	12
	Cathode Layers	7
Anode	Material	Li
	Areal Capacity (mAh/cm^2 each side of Cu)	10
	Cell Balance (N/P ratio)	2.6
	Electrode thickness(each side of Cu) (µm)	50
	Cu foil thickness (µm)	8
Electrolyte	Electrolyte/capacity (g/Ah)	3.1
	Weight (g)	3.3
Separator	Thickness (µm)	20
Packaging Foil	Thickness (µm)	115
Pouch Cell	Voltage (V)	3.8
	Capacity (Ah)	1.07
	Energy density (Wh/Kg)	300

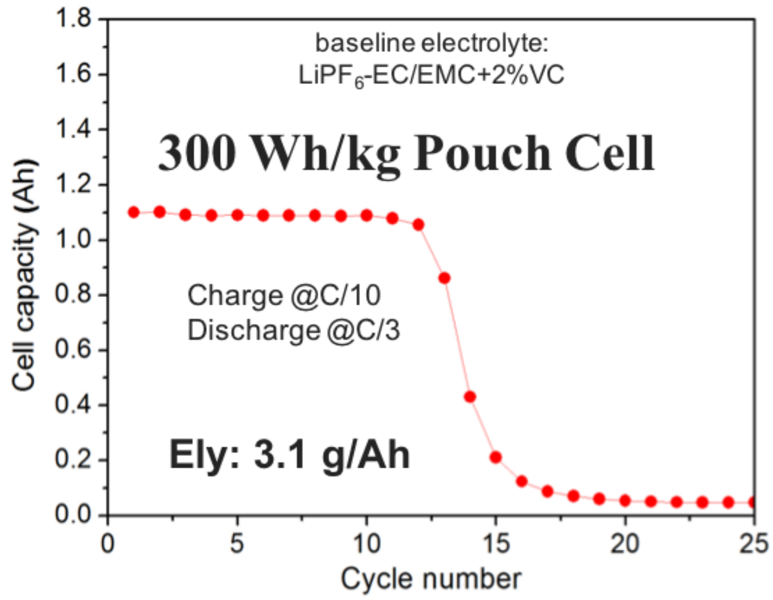


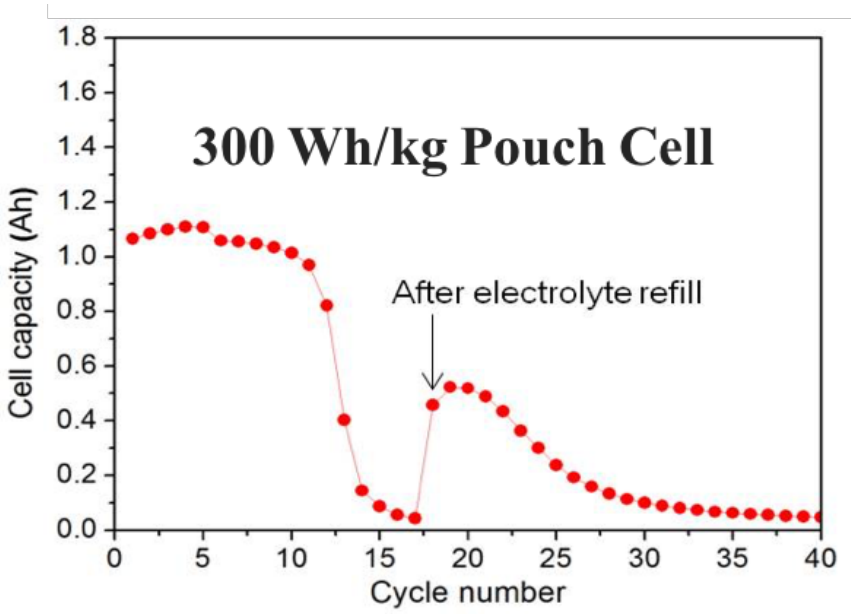
- Appropriate cell designs guide the fabrication of pouch cells with different energy/power and cycling requirements.
- Cathode areal capacity, N/P ratio and electrolyte content are interrelated parameters that dynamically impact the cell energy and cycling stability simultaneously.

BATTERY 500 CONSORTIUM

Technical Accomplishments
Li/NMC622 Pouch Cells Have Very Limited Cycling in Carbonate-based Electrolyte

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



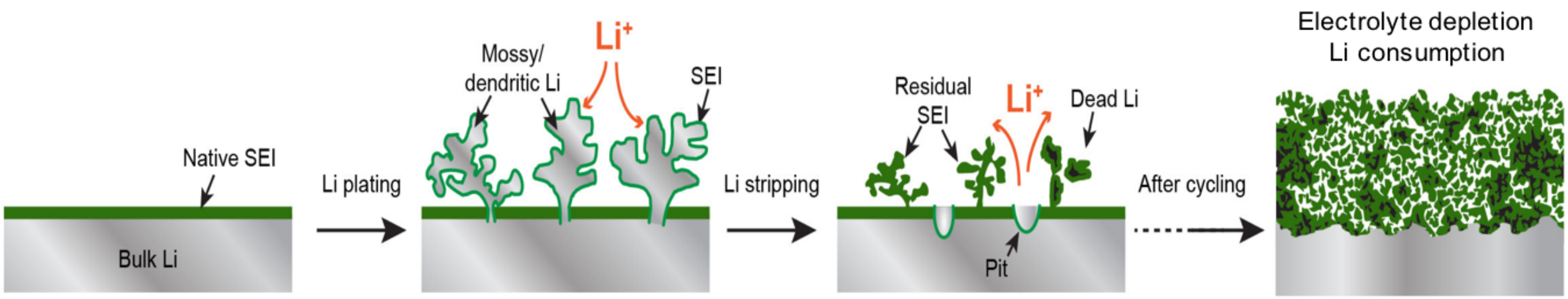


- Pouch cell capacity always ”dives” after 12 cycles regardless of electrolyte amounts.
  - NMC622 cathodes still works well in re-assembled cells (backup slide)
  - Cell is not short as reflected by the voltage profiles after failure (backup slide).
- Refilling electrolyte only partially recovers the capacity.
  - Electrolyte drying out is NOT the only reason for fast capacity decay.
  - Li is also being depleted after 15 cycles!

BATTERY 500 CONSORTIUM

Technical Accomplishments
SEI Formation Consumes both Electrolyte and Li

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*



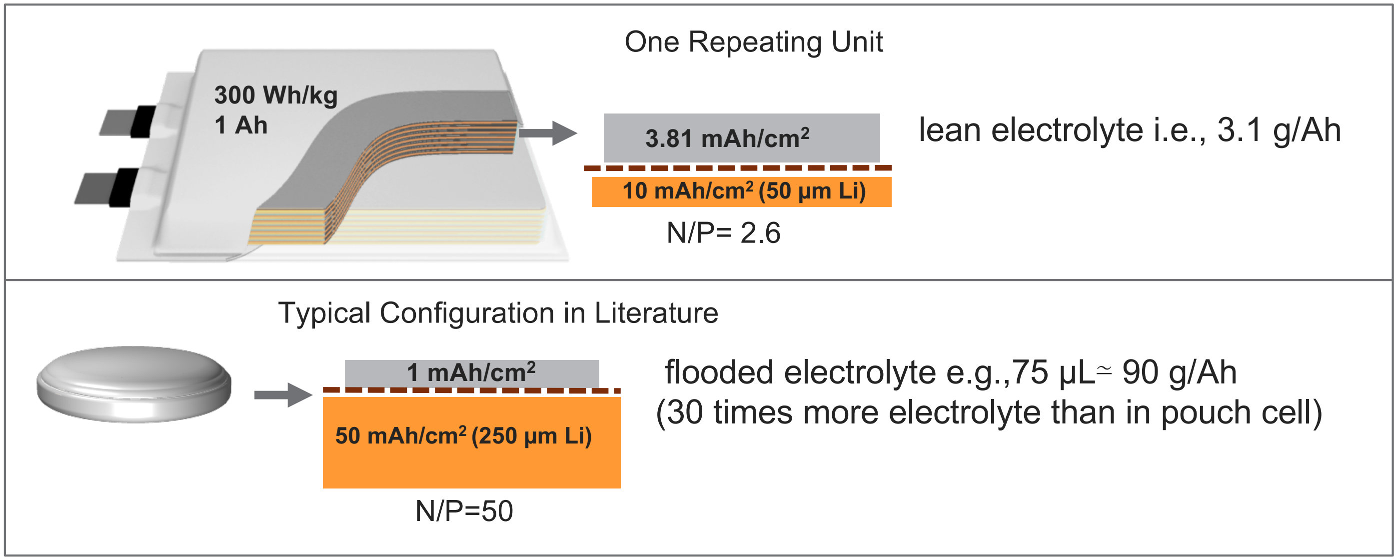
- Electrolyte is continuously consumed to form SEI on newly exposed Li surfaces.
- Part of Li is tightly "wrapped" by insulating SEI layers and loses electronic contact with anode: "dead" Li formation
- "Dead" Li is continuously accumulated during cycling: Li depletion

BATTERY 500 CONSORTIUM

Technical Accomplishments

Li and Electrolyte Contents are Drastically Different in High- Energy Pouch Cells and Lab-testing Coin Cells

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



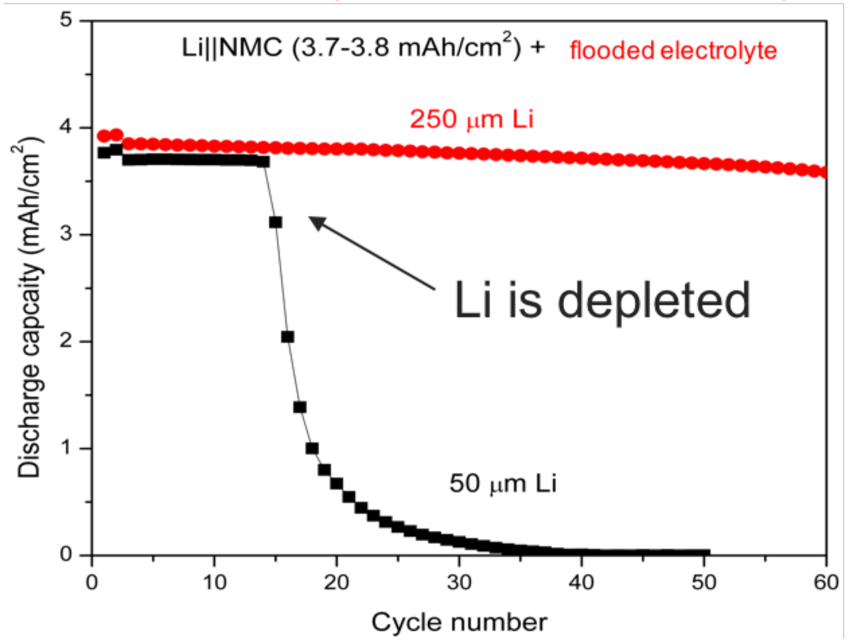
- During each cycle: both electrolyte and Li are irreversibly consumed
  - Pouch cells: very restricted amounts of Li and electrolyte so the cell degrades very fast
  - Coin cells: almost unlimited amounts of Li and electrolyte thus hundreds of stable cycling is often seen in literature
- A standard coin cell testing protocol has been developed to close the gap between coin cell evaluation and pouch cell fabrication.

BATTERY 500 CONSORTIUM

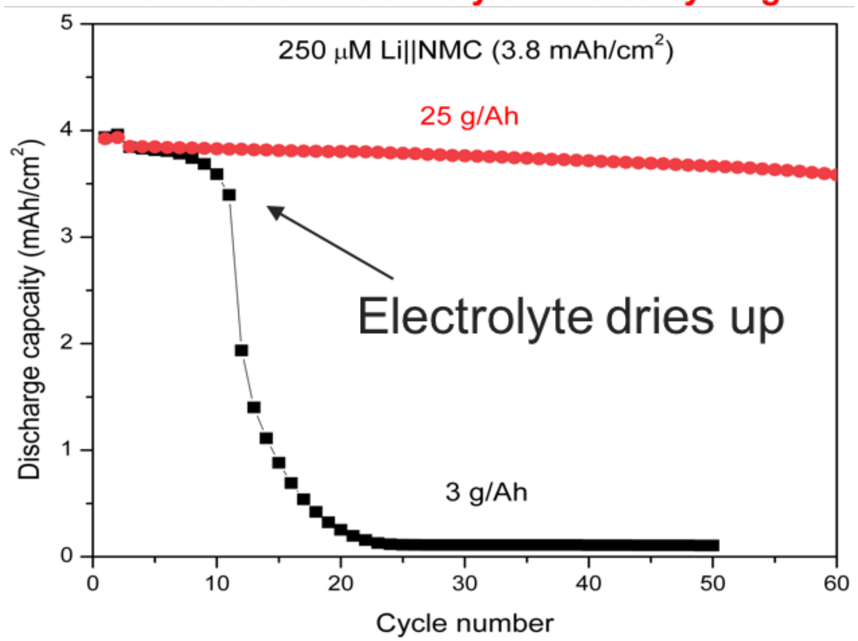
Technical Accomplishments
Both Li and Electrolyte Contents Significantly Impact Cycling Stability of Li Metal Cells

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

sufficient electrolyte: Li amount determines cycling



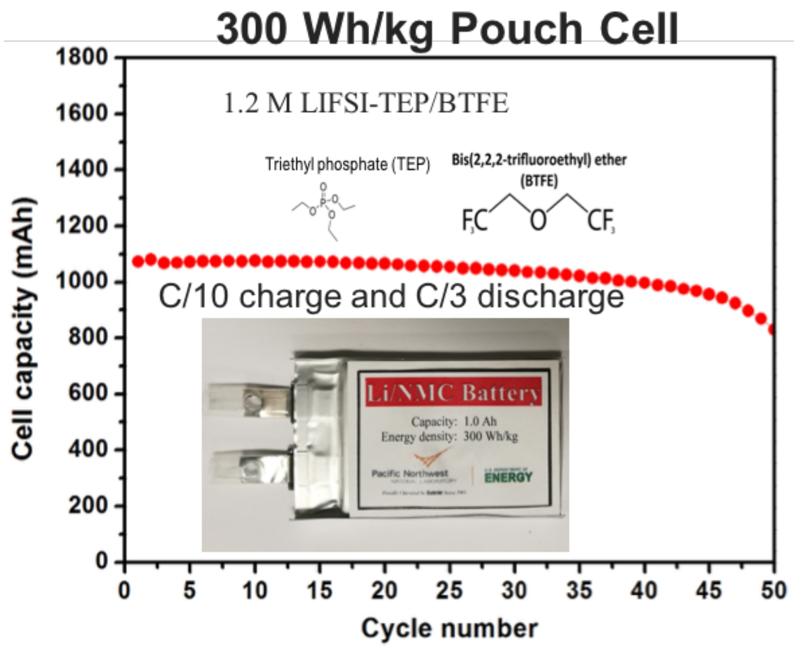
sufficient Li: electrolyte dictates cycling

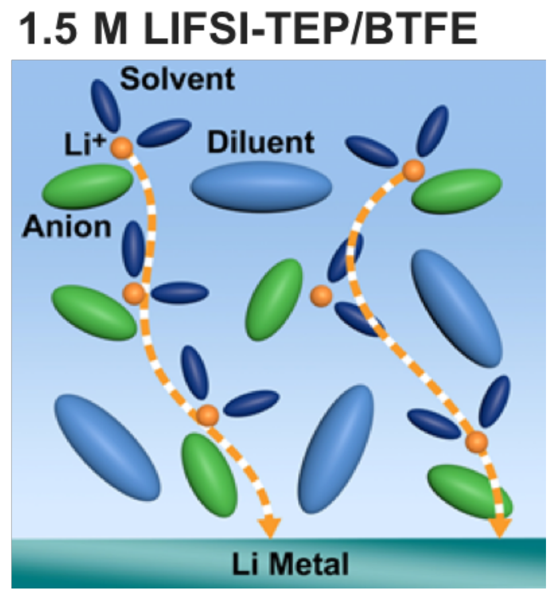


- Cells are terminated once Li or electrolyte (or both) is completely drained, whichever comes first.
- Pouch cells consist of thin Li (50 um) and lean electrolyte (3 g/Ah)
- Confirm that the continuous consumption of thin Li and lean electrolyte leads to fast pouch cell degradation.

BATTERY 500 CONSORTIUM

Technical Accomplishments
New Electrolyte Mitigates Side Reactions between Li and Electrolyte





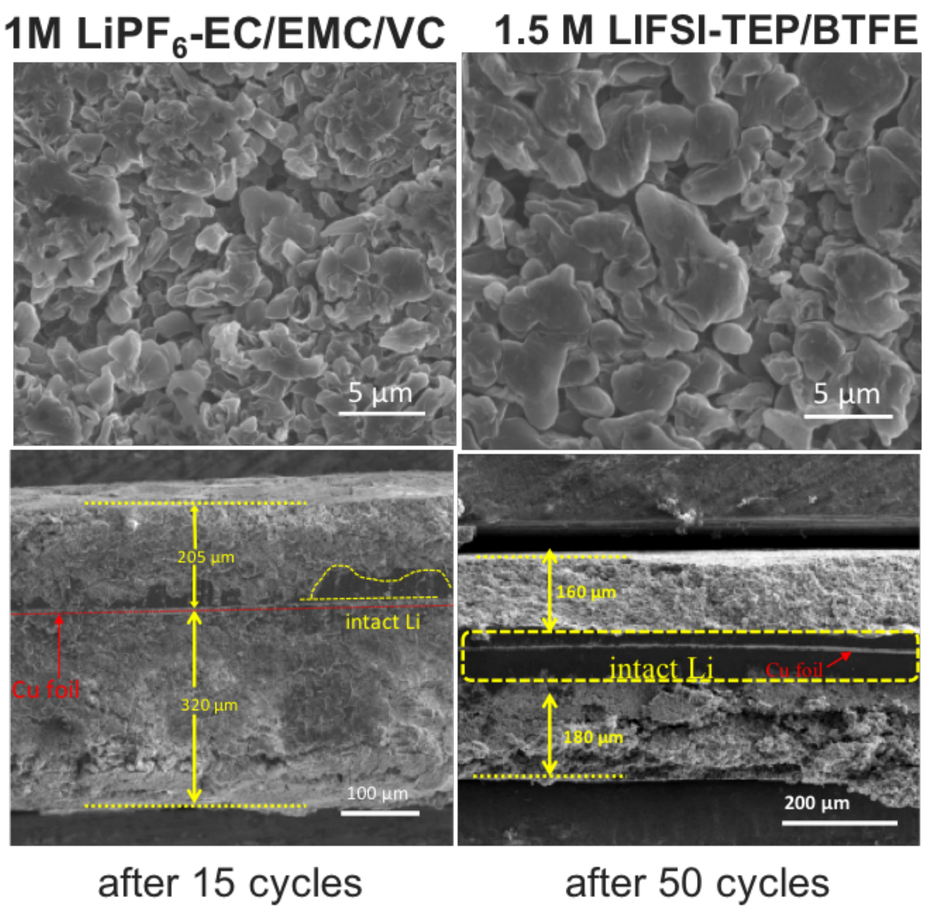
* *J.-G.Zhang et al, Advance Materials, 2018, DOI: 10.1002/adma.201706102*

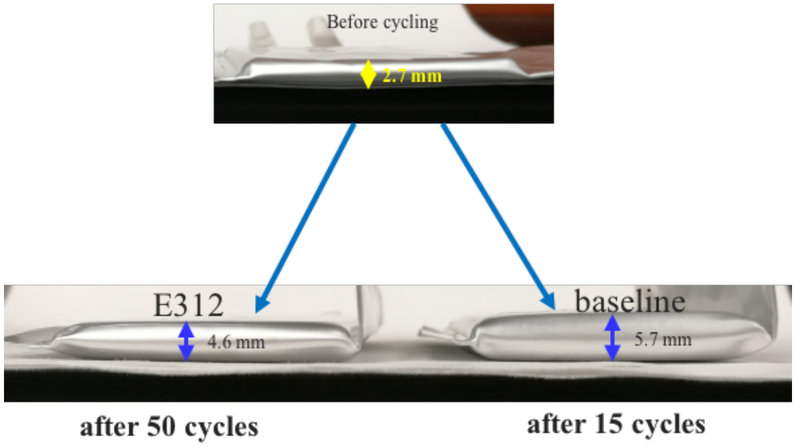
- New electrolyte (1.5 M LiFSI-TEP/BTFE) greatly extends pouch cell lifespan (project #Bat362).
  - Less amount of electrolyte and Li are consumed each cycle
  - Improved SEI quality to slow down "dead" Li formation
  - Non-flammable, low viscosity and good wetting
- Independent pouch cell testing at INL demonstrated > 100 stable cycles (project # Bat368)

Technical Accomplishments

New Electrolyte Slows Down the Side Reactions between Thin Li and Lean Electrolyte

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



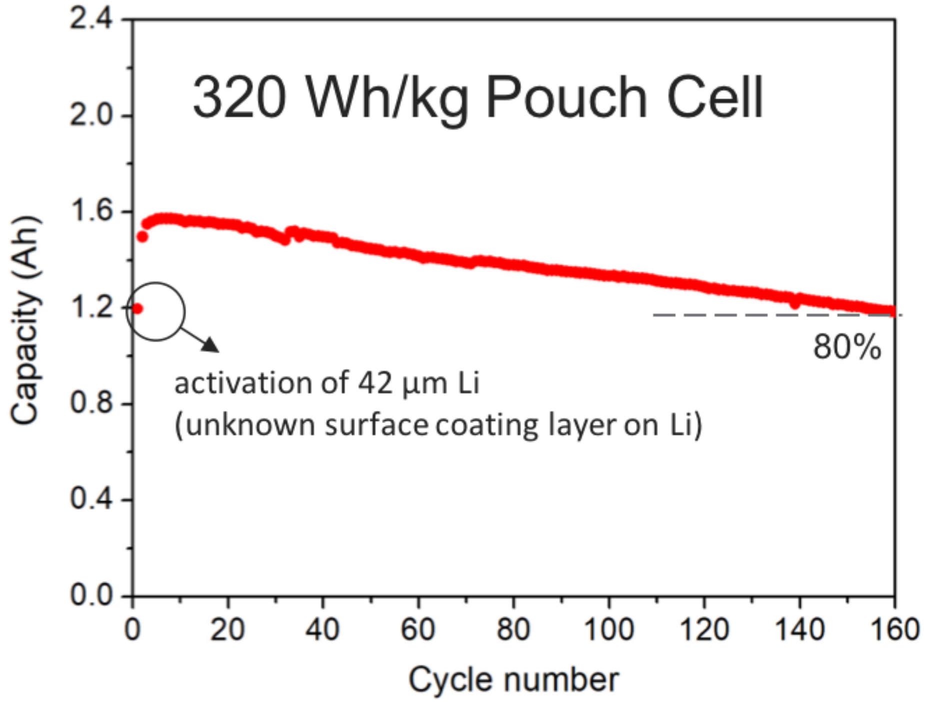


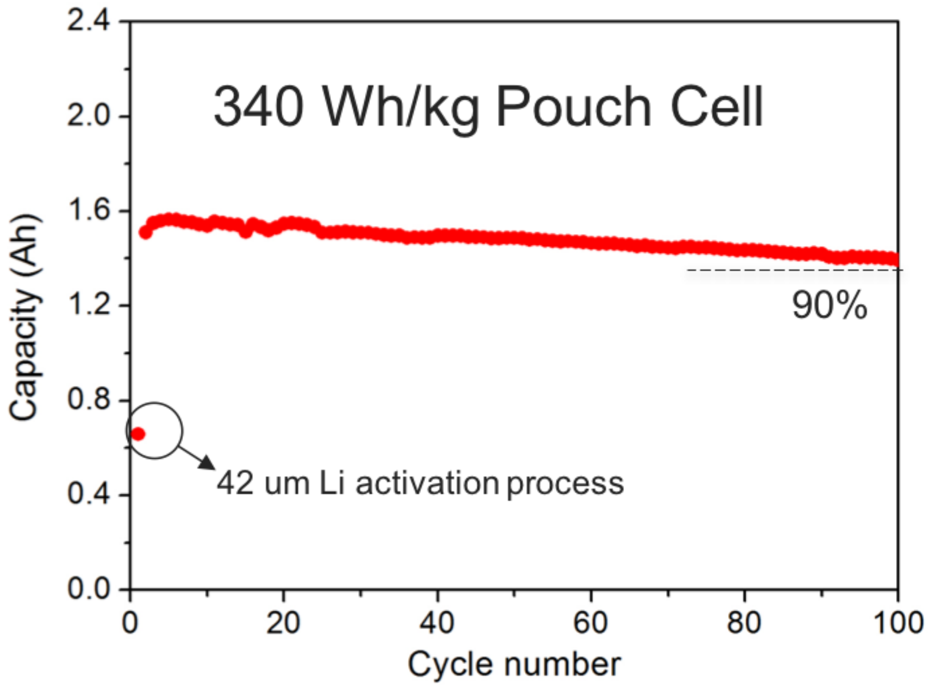
- In new electrolyte (300 Wh/kg cell):
  - Cycled Li has larger average particle sizes: less surface areas for side reactions.
  - Li shows less expansion and cell volume expansion is also reduced.
  - No uniform external pressure applied yet in both tests.
- Intact Li is found in the cell tested in new electrolyte.

BATTERY 500 CONSORTIUM

Technical Accomplishments
New Electrolyte is also Compatible with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) Cathode

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965





Testing conditions:
first 2 cycles: C/10 for charge/discharge
subsequent cycles: C/10 charge and C/3 discharge

- Li/NMC811 chemistry further increases cell energy to > 300 Wh/kg.
- Optimized cell design is critical to extend stable cycling to beyond 100 cycles.

BATTERY 500 CONSORTIUM

Responses to Previous Years Reviewers' Comments

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

- This project was not reviewed last year.

BATTERY 500 CONSORTIUM

Collaboration and Coordination with Other Institutions

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Industry:
  - General Motors: independent testing of PNNL's thick S electrodes
  - Navitas System: new coating method
- University:
  - UT Austin: Supplied high-Ni NMC to PNNL for evaluation
  - Univ. Washington: separator coating
  - SUNY Binghamton: cell fabrication
  - UC San Diego: testing on industry-made electrodes and PNNL electrolytes
  - Univ. Pittsburg: supplied S/C composite for electrode coating
  - Penn State Univ.: testing of thick NMC and S electrodes made
  - Univ. Houston: testing of PNNL new electrolyte
  - Stanford: S electrodes testing
  - Univ. Maryland/Army research Lab: electrolyte development
- National Laboratory
  - Idaho National Lab: independent testing of PNNL-made pouch cell
  - Brookhaven Nation Lab: characterization of PNNL fabricated electrodes/electrolytes
  - SLAC: new electrolyte characterization

BATTERY 500 CONSORTIUM

Remaining Challenges and Barriers

- Push the cell energy towards 500 Wh/kg by appropriate cell designs and new electrolytes
- Balance of high energy and cycle life of Li metal cells
- Dendrite-induced cell shorting (C/10 charging rate is used in FY18 to decouple cell shorting and cell failure caused by Li/electrolyte depletion.)

Proposed Future Work

- FY18 (Q4): **Demonstrate 350Wh/kg pouch cell with >50 stable cycling and <20% fading**
- FY19:
  - Cell design to balance energy and cycling
  - Optimization of the new electrolyte to further enhance the cycling stability of Li/NMC811 pouch cells
  - Electrolyte and separator modifications to improve Li-S pouch cell cycling ability
  - Li metal modification to improve the anode stability

Any proposed future work is subject to change based on funding levels.

Summary

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

- ≥300 Wh/kg Li metal pouch cells have been successfully fabricated and demonstrated >100 stable cycling.
- Cell-level fundamentally new challenges are identified.
  - Pouch cells contain very limited amounts of Li and electrolyte.
  - The fast depletion of both Li and electrolyte leads to the quick cell degradation.
- New electrolyte has been developed to enhance Li stability and is also compatible with high-Ni NMC cathodes.
- A standard coin cell testing protocol has been developed and shared across the team to accelerate innovations at relevant scales.

BATTERY 500 CONSORTIUM

Acknowledgement

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

- DOE/EERE/VTO: Battery500
- Key contributors: C. Niu, D. Lv, S. Chen, H. Lee, X. Ren, S.Q. Wilson, Q. Li, W. Xu and J. Zhang
- Battery500 PIs and their teams

BATTERY 500 CONSORTIUM